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Direct 17O Dynamic Nuclear Polarization of Single-Site Heterogeneous Catalysts

Frederic A. Perras
Ames Laboratory, fperras@ameslab.gov

Kasuni Chathurika Boteju
Iowa State University and Ames Laboratory, kasuni@iastate.edu

Igor Ivan Slowing
Iowa State University and Ames Laboratory, islowing@iastate.edu

Aaron D. Sadow
Iowa State University and Ames Laboratory, sadow@iastate.edu

Marek Pruski
Iowa State University and Ames Laboratory, mpruski@iastate.edu

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Abstract
We utilize direct 17O DNP for the characterization of non-protonated oxygens in heterogeneous catalysts. The optimal sample preparation and population transfer approach for 17O direct DNP experiments performed on silica surfaces are determined and applied to the characterization of Zr- and Y-based mesoporous silica-supported single-site catalysts.

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Direct ^{17}O Dynamic Nuclear Polarization of Single-Site Heterogeneous Catalysts

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Frédéric A. Perras,[a] Kasuni C. Boteju,[ab] Igor I. Slowing,[ab] Aaron D. Sadow,[ab] and Marek Pruski*[ab]

We utilize direct ^{17}O DNP for the characterization of non-protonated oxygens in heterogeneous catalysts. The optimal sample preparation and population transfer approach for ^{17}O direct DNP experiments performed on silica surfaces are determined and applied to the characterization of Zr- and Y-based mesoporous silica-supported single-site catalysts.

The characterization of the surfaces of heterogeneous catalysts is one of the most challenging endeavors in structural science. The lack of periodicity precludes the use of diffraction techniques, whereas the low concentration of the surface sites, often accompanied by the overwhelming presence of bulk sites, severely limits the applicability of solid-state nuclear magnetic resonance (SSNMR) spectroscopy. Recently, dynamic nuclear polarization (DNP) has emerged as a means of sensitizing SSNMR experiments performed on surface species; an approach called DNP surface-enhanced NMR spectroscopy (DNP SENS).[1] Briefly, in a DNP SENS experiment, the surface of the material is coated with a radical-containing solution, by using incipient wetness impregnation, and irradiated with high-power microwaves at the electron's Larmor frequency to promote a polarization transfer from the electron spins to the nuclear spins. This process can, in theory, enhance the SSNMR spectra by as much as γ_e/γ_n, which equals 658 for ^{1}H. Indeed, DNP SENS has dramatically amplified the NMR responses from a variety of unreceptive nuclei, allowing characterization of previously undetectable surface-supported functional groups and metal catalysts,[2] and determination of their distributions[3] as well as three-dimensional conformations at the surface.[4]

DNP SENS has notably enabled the detection of ^{17}O under its natural abundance of only 0.038%, such detection is beyond the practical capabilities of conventional SSNMR.[5] In the field of catalysis, however, DNP SENS studies on naturally ^{17}O-abundant samples have been thus far limited to surface hydroxyls and Brønsted acidity.[6] This limitation is the case because indirect DNP, currently the most convenient and sensitive incarnation of DNP SENS, relies on the ^{1}H spins being directly hyperpolarized. The ^{1}H hyperpolarization must then be transferred to ^{17}O using a subsequent cross-polarization (CP)[5,7] or PRESTO (phase-shifted recoupling effects a smooth transfer of polarization)[6] step. The indirect approach relies on close proximity between ^{1}H and ^{17}O nuclei, typically less than 2 Å. This major shortcoming precludes its use for characterization of non-protonated surface oxygens, such as those directly coordinating the metal centers in single-site catalysts. Direct DNP, involving a radical-to-heteronuclei sensitization scheme, is needed to alleviate this constraint.[5,8,9] In this work we assess the sensitivity gains achievable for silica surfaces by direct ^{17}O DNP SENS and apply this approach to the first characterization of single-site catalysts.

The most commonly used radical polarizing agents are dinitroxides, as these have a suitable EPR linewidth to mediate the efficient 2-electron/1-nucleus DNP mechanism known as the cross-effect.[10] Michaelis has, however, shown that narrow-line trityl radicals outperformed dinitroxides for ^{17}O direct DNP at a low magnetic field of 5 T.[8a] Alternatively, the state-of-the-art dinitroxide polarizing agent TEKPol[11] has been used in direct DNP SENS experiments on ceria.[8b] We have thus decided to compare the efficacy of trityl and TEKPol for the hyperpolarization of ^{17}O in SBA-type mesoporous silica nanoparticles (MSNs). The tests were performed on a sample referred to as ^{17}O-MSN, which was enriched with ^{17}O to ~20% using the method of Merle et al. (see the ESI for details);[12] this method selectively enriched the surface of the MSN. As can be seen by comparing the top 2 spectra in Figure 1, TEKPol yielded a ^{17}O direct DNP enhancement (ε_{DNP}) of 16, which was 4 times greater than the ε_{DNP} afforded by trityl in water. The greater performance of TEKPol may be caused by its more favorable affinity toward the silica surface, which would lead to a greater association of the radical with the material,[13] the higher magnetic field used in this study (9.4 T) which may have led to a quenching of the cross-effect mechanism in trityl, and/or the application of MAS (previous experiments were

[a] US DOE, Ames Laboratory, Ames, IA 50011, USA.
[b] Department of Chemistry, Iowa State University, Ames, IA 50011, USA.
[c] E-mail: mpruski@iastate.edu
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performed on static samples[8a]). An AMUPol[14]/$H_2{}^{16}O$ solution provided a similar performance to TEKPol/TCE (see Figure S3), demonstrating that the solvent is not the determining factor. The superior performance of the TEKPol/TCE solution is also fortuitous since the use of water as a solvent may lead to undesirable hydrolysis and the degradation of metal catalysts.

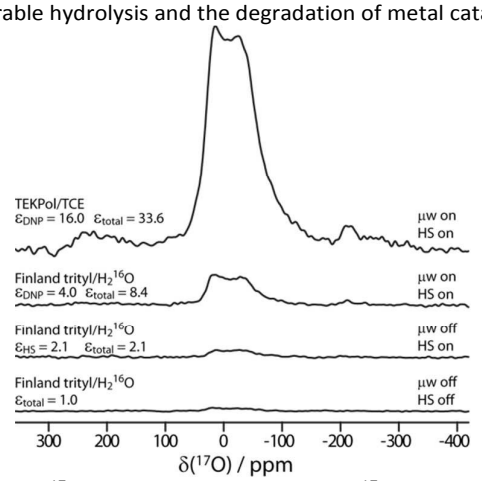

Figure 1. ^{17}O MAS SSNMR spectra of ^{17}O-MSN. The top spectrum was acquired for a sample impregnated with 16 mM solution of TEKPol in TCE. The lower 3 spectra were taken using 40 mM solution of Finland trityl in $H_2{}^{16}O$. Labels are added on the right side of the spectra to indicate whether HS or DNP is used to enhance a particular spectrum. The enhancement factors are listed on the left side of the spectra, demonstrating the highest performance of TEKPol; ε_{DNP} represents the signal enhancement measured by performing measurements with and without microwave irradiation.

One of the advantages of performing direct ^{17}O DNP, as opposed to indirect DNP, is that secondary sensitivity enhancement techniques that transfer polarization from the satellite transitions to the observed central transition (m = ½ to -½)[15] can be used alongside the electron-nucleus transfer to augment the sensitivity.[5] We have therefore examined the utility of the double-frequency sweep (DFS)[16] and hyperbolic secant (HS)[17] polarization transfer methods for direct DNP experiments on silica samples. Due to its wide and non-selective sweeps, DFS is generally the more robust of the two techniques[18] (and has been used to characterize single-site catalysts[19]), while HS usually leads to greater sensitivity enhancements.[15] Indeed, we were able to enhance the ^{17}O siloxane resonance in ^{17}O-MSN by 2.1 with HS (Figure 1) and 1.8 with DFS (spectrum not shown). When combining HS with DNP, we achieved the total enhancement ε_{total} = 33.6.

The importance of direct ^{17}O DNP is exemplified in Figure 2 by comparing the spectra acquired on the very same ^{17}O-MSN sample using direct and indirect ^{17}O DNP (with PRESTO-II[20]). Note that the two experiments carry different information; while only the silanols are selectively polarized in the indirect DNP experiment, all sites are present in the direct DNP spectrum, which is accordingly dominated by the more numerous siloxanes. Remarkably, the maximum signal intensity in the indirect DNP experiment is only 13% higher than in the direct DNP experiment. This is the case since although the indirect DNP enhancement is considerably higher (ε_{DNP} = 180), the silanols are less concentrated. When considering that the ^{17}O relaxation times are longer (2.4 s) than the ^{1}H relaxation times (1.3 s), the indirect DNP experiment has a sensitivity, per unit of time,[21] that is only approximately 50% greater than the direct DNP experiment. It should thus be possible to detect highly-concentrated sites, such as siloxanes, at natural abundance using direct DNP.

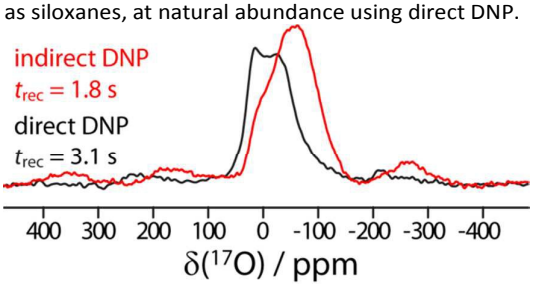

Figure 2. The ^{17}O direct DNP (black) and indirect DNP (red) spectra of ^{17}O-MSN acquired using the same number of scans. t_{rec} refers to the recycle delay used.

Since the optimal magnetic fields for ^{1}H and ^{17}O DNP are only separated by 500 ppm,[8] hyperpolarization of ^{1}H nuclei could diminish the enhancement of ^{17}O signal. Thus, we investigated whether the use of fully deuterated solvents[22] (here 1,1,2,2-tetrachloroethane, TCE) could provide additional sensitivity in ^{17}O direct DNP SENS experiments. A freshly-dried ^{17}O-enriched MSN was used in these experiments, for which a ^{17}O direct DNP enhancement of 22 (ε_{total} = 46) was obtained with protonated TCE, and a slightly higher enhancement of 27 (ε_{total} = 57) was obtained with (^{2}H)TCE (see Figure 3). Similarly to solvent deuteration, drier MSNs show higher direct DNP enhancements due to a reduced ^{1}H concentration. High ^{1}H abundance may also have been one of the contributing factors in the low performance of the trityl/$H_2{}^{16}O$ solutions.

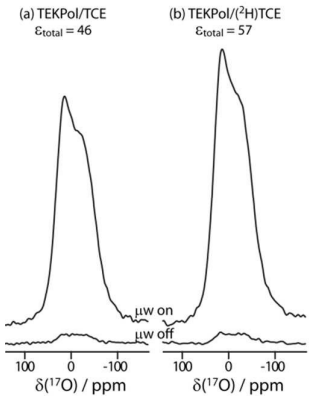

Figure 3. ^{17}O MAS SSNMR spectra of a freshly-dried ^{17}O-MSN impregnated with 16mM TEKPol solutions in TCE (a) and (^{2}H)TCE (b). A slightly greater DNP enhancement can be obtained by using a deuterated solvent.

Lastly, we applied ^{17}O direct DNP-enhanced SSNMR spectroscopy for the characterization of silica-supported single-site catalysts. For this purpose, we chose to study our

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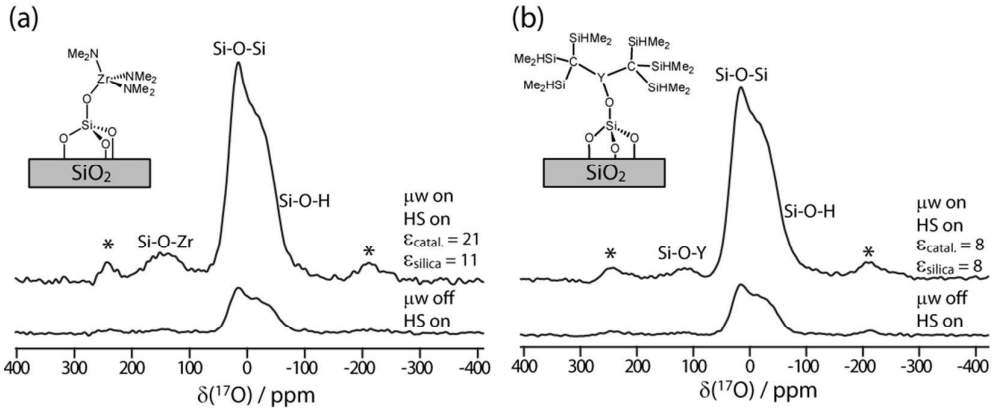

Figure 4. ^{17}O direct DNP-enhanced SSNMR spectra of the Zr(NMe$_2$)$_n$@MSN (a) and Y{C(SiHMe$_2$)$_3$}$_n$@MSN (b) catalysts are shown along with the postulated structures of each catalyst. Also shown are the spectra acquired without microwave irradiation and the total enhancement factors for the silica and ligated ^{17}O resonances. In all spectra, HS was used to enhance the sensitivity.

previously-published Zr(NMe$_2$)$_n$@MSN catalyst for the hydroboration of aldehydes and ketones,[23] as well a Y{C(SiHMe$_2$)$_3$}$_n$@MSN species[24] which will be described in greater detail in a later publication. To avoid the degradation of the catalysts, the samples were packed in a glovebox using dry (^{2}H)TCE. First, we have confirmed by ^{13}C DNP-enhanced SSNMR that both catalysts remained intact upon the addition of the 16mM TEKPol solution in TCE used in this study (see ref. 23 and Figure S1). The ^{17}O direct DNP-enhanced SSNMR spectra of these catalysts are shown in Figure 4. In both cases it is possible to clearly distinguish the resonances from the siloxanes as well as those from the oxygen sites that link the catalyst to the surface. The interactions with the metal sites shift the former silanol's resonances to considerably higher frequency; 145 ppm in the case of the Zr catalyst and 115 ppm in the case of the Y catalyst. These shifts, which correspond to the sum of the chemical shift and second-order quadrupole-induced shift, are in agreement with the trend that oxide chemical shifts are inversely correlated to the polarizing power (r^2/z, where r = cation radius and z = charge) of the metal site to which oxygen is coordinating.[25]

Unfortunately, the ε_{total} values decreased after grafting of the Zr and Y catalysts to 11 and 8 for the siloxane, and to 21 and 8 for the ligated oxygen's resonances, respectively. This drop is likely caused by the increased ^{1}H density at the surface and the presence of methyl groups in the two catalysts.[26] Interestingly, in the case of the Zr catalyst, the enhancement factor for the ligated oxygen was twice as high as for the siloxanes. One possible explanation for this difference is that the catalyst is situated exclusively at the surface, near the polarizing agent, while the siloxane can also be found in the bulk. A higher enhancement was not observed for the ligated oxygen site in the case of the yttrium complex, perhaps due to its bulkier ligands limiting the access to the oxygen.

Upon grafting of the catalyst, the DNP build-up rate increased to approximately 7.5 s and thus the time sensitivity[21] for the detection of the catalyst resonance was 1.4% that of the indirect DNP experiment from Figure 2, in the case of the Zr catalyst, and 0.5% that of the indirect DNP experiment for the Y catalyst. It is thus currently not possible to detect these sites at natural abundance using direct DNP. Direct DNP can nevertheless shorten the ^{17}O studies of catalysts 100-fold and enable previously inaccessible ^{17}O SSNMR experiments.

In summary, we have assessed the efficacy of ^{17}O direct DNP for the characterization of unprotonated oxygen sites in silica-supported single-site catalysts. For bare ^{17}O-MSNs, total sensitivity enhancements of up to 57 were obtained through the combined use of DNP, with TEKPol in a deuterated solvent as polarization agent, and HS to boost the polarization of the central transition. The sensitivity of these experiments rivaled the indirect DNP which has earlier proven competent on natural abundance samples. Sizeable, albeit lower, enhancements could be obtained on single-site catalysts, enabling the observation of all oxygen species, including the link between the catalyst and the support, and a shortening of ^{17}O SSNMR experiments by two orders of magnitude. Future advances in methodology will undoubtedly enable the acquisition of such spectra on natural abundance samples.

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Conflicts of interest

There are no conflicts to declare.

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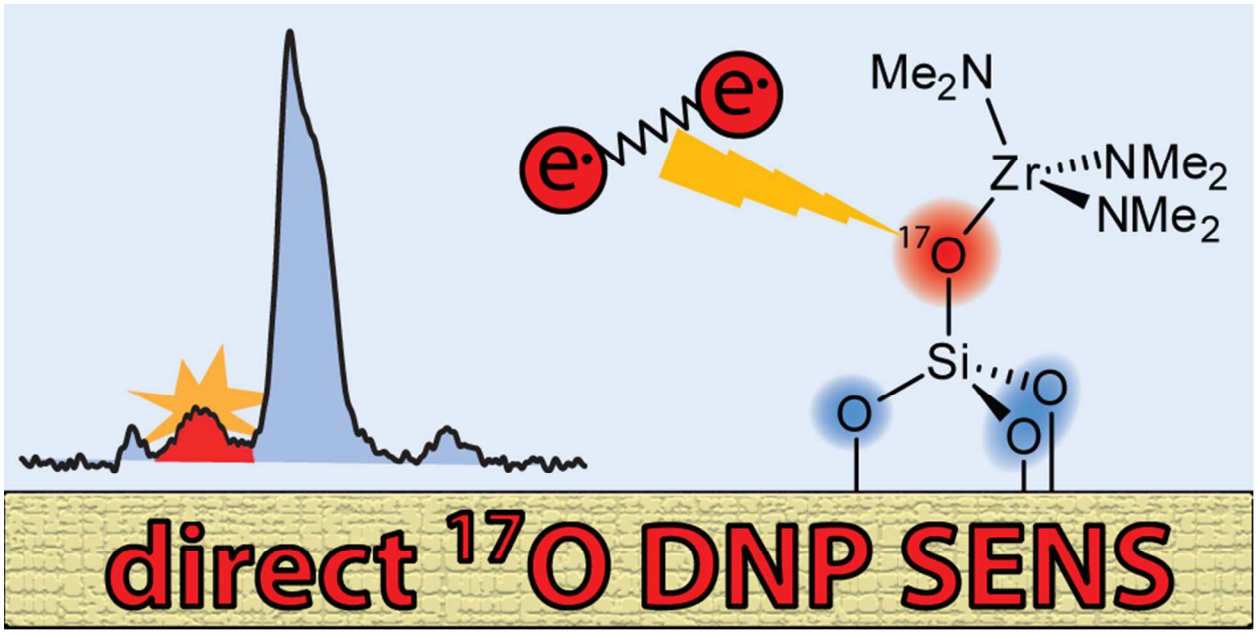

Direct DNP is shown to effectively enhance ^{17}O signals from non-protonated binding sites for surface-supported catalysts.